

The Influence of Electrical Parameters on Selectivity of Electrochemical Fluorosulfation of Fluoroolefins

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The electrochemical fluorosulfation of fluoroolefins both terminal and - is a convenient method of preparation of fluoroalifatic fluorosulfates which in their turn are starting materials in the synthesis of various classes of fluoroalifatic compounds. As a rule the electrochemical fluorosulfation is carried by subjecting the mixture of fluoroolefine and fluorosulfuric acid to electrolysis under the high anodic potentials. Peroxodisulfuryldifluoride (I) formed as a result of fluorosulfonyloxy-anion electrooxidation reacts with fluoroolefine; current efficiency of (I) is 60-65

2FSO₃ - 2e (FSO₃)₂

Indirect electrochemical fluorosulfation of fluoroolefins

The interaction of (I) with fluoroolefins has a clear radical character. The products obtained consist of a mixture of vicinal bis-fluorosulfates (adducts of composition 1:1) and the products of fluorosulfatodimerisation of starting fluoroolefins. The results of interaction of higher branched fluoroolefins ((CF₃)₂CR₁CF=CFCF₃; R=F (II), R=CF₃ (III)) with (I) fall out from a general rule: the vicinal fluorosulfates were the only reaction products. Obviously the absence of corresponding fluorosulfatodimers is connected with a structural peculiarities of these olefins. The stable bis-diperfluoroalkylmethyl radicals (CF₃)₂CR₁CFCF(OSO₂F)CF₃ formed were registered by EPR technique. Such radicals are capable of adding the second fluorosulfonyloxy radical but can not dimerize. In the course of investigation of the electrochemical fluorosulfation of unsaturated perfluorinated ketons and fluoroanhydrides (CF₃)₂CR₁CF=CFC(O)R₁; R₁=F (IV), R₁=C₂F₅ (V) the structural analogs of olefine (II) it was found that the vicinal bis-fluorosulfates and fluorosulfatodimers of starting olefins were formed [1]. The products of the reaction of diene i-C₃F₇CF=CFCF=CFCF₃-i. (VI) with electrochemically generated (I) are especially interest. The adduct (1:1) obtained along with fluorosulfatodimers contained fluorosulfonyloxy groups not at a,b-, but at a,d- positions. It was shown that the addition of fluorosulfonyloxy radical to sterically hindered vinyl C-atom leads to generation of allyl or heteroallyl radicals and therefore the composition of the products of the electrochemical fluorosulfation reflects the competition of the sterical and electronic factors which determine the direction of the radical attack.

Direct electrochemical fluorosulfation of fluoroolefins

At the same an alternative approach to electrochemical fluorosulfation of fluoroolefins can be considered : it is a direct anodic oxidation of olefins under the potentials less positive than FSO₃- anion electrooxidation with a consequence of electrochemical and chemical EC- and/or ECEC stages. The composition of

the reaction products will be determinate by the ratio of the processes rates occurring directly at the surface of the electrode and in the solution bulk. It was shown that the composition of the electrolysis products changed dramatically in the course of fluorosulfation of lower fluoroolefins under different electrolysis conditions. For example the fluorosulfation of tetrafluoroethylene on Pt and glassy carbon electrodes under the conditions of (I) formation affords mainly 1,4-bis-fluorosulfonyloxy-perfluorobutane. Under the conditions of potentiostatic electrooxidation of tetrafluoroethylene at the potential of anode 1.3-1.5 V the main product of the reaction was 1,2-bis-fluorosulfonyloxyperfluoroethane [2]. It was established that the other olefins can be also oxidized at the potentials less positive than the potential of FSO₃- anion electrooxidation [3], that permits to carry out their selective fluorosulfation. Cyclic voltammetry of olefins (IV, V, VI) showed that fluorosulfation according to ECEC mechanism can be realize only in the case of diene (VI).

The preparative electrolysis of VI on glassy carbon electrode at the potential 1.75 V led to the formation of i-C₃F₇CF(OSO₂F)CF=CFCF(OSO₂F)C₃F₇-i (VII) as the only product of the reaction. Fluorosulfatodimer has not been detected at all. The comparison of the results of the electrochemical fluorosulfation of unsaturated fluorocarbons under the conditions of indirect and direct fluorosulfation shows that the potentiostatic conditions lead to the formation of vicinal fluorosulfates as a main or only products. The high rate of the second electrochemical step exceeding the rate of the desorption of intermediate radical from the electrode surface into the solution bulk leads to the grows of the share of vicinal bis-fluorosulfates thus increasing the overall selectivity of the process.

References

1. S. R. Sterlin., B. L. Tumanskii., E. N. Shaposhnikova, et al, *Izv. AN, ser. khim.* 11, 2207 (1999). (in Russian)
2. V. A. Grinberg, Yu. B. Vassiliev, *J. Electroanal.Chem.* 325, 185 (1992).
3. V. A. Grinberg, S. R. Sterlin, V. F. Cherstkov, *Elektrokhimija* 29, 396 (1993). (in Russian)